Dielectric nonlinearity of relaxor ferroelectric ceramics at low ac drives

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Abstract

Dielectric nonlinear response of $(PbMg_{1/3}Nb_{2/3}O_3)_{0.9}(PbTiO_3)_{0.1}$ (0.9PMN-0.1PT) relaxor ceramics was investigated under different ac drive voltages. It was observed that: (i) the dielectric permittivity is independent on ac field amplitude at high temperatures; (ii) with increasing ac drive, the permittivity maximum increases, and the temperature of the maximum shifts to lower temperature; (iii) the nonlinear effect is weakened when the measurement frequency increases. The influences of increasing ac drive were found to be similar to that of decreasing frequency. It is believed that the dielectric nonlinearities of relaxors at low drives can be explained by the phase transition theory of ergodic space shrinking in succession. A Monte Carlo simulation was performed on the flips of micro polarizations at low ac drives to verify the theory.

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I. INTRODUCTION

Since $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) was first synthesized by Smolenski *et al.* in the late 1950s,[1] there has been a series of relaxor ferroelectrics (relaxors) with complex perovskite structure whose dielectric and ferroelectric properties are rather different from that of normal ferroelectrics. For the relaxor ferroelectrics, the dielectric permittivity is unusually high, the sintering temperature is rather low, and the temperature coefficient of capacitance is quite small due to the diffuse phase transition (DPT), which lead to the successful application as Multi-layered Capacitors (MLC).[2] In addition, the field-induced piezoelectric effect of relaxors is strong, and the pulse echo response of transducer can be controlled by bias voltage. So the relaxors are competent in the range of actuators, medical diagnostic transducers, etc..[3,4] Recently, the observation of the highly excellent electromechanical properties in some single crystal of relaxors (for example, the PMN-PT solid solution) has brought great interest to the research, development and application of this kind of materials.[5]

In actual applications, the components and device made of relaxors usually work under dc bias or ac drive voltages. So the performances of the material under external field always cause great interests. In recent years, some works focus on the dielectric nonlinear response under various ac drive voltages. Apart from the strong application background, these works can also provide some clues of the polarization mechanism of relaxors in theory. Although several possible models have been proposed, the nature of the dielectric response of relaxors, especially PMN, keeps unclear.[6] Experiments such as high-resolution transmission electron microscopy (HTEM) have confirmed a main feature of PMN in structure: a great amount of nanoscaled ordered microregions are embedded randomly in the disordered matrix.[7,8] The ordered microregions are probably nonstoichiometric.[8] The assumption that the ordered microregions are just the centers of polar microregions presented by the superparaelectric model[9] need further testification of experiments, but the theoretical calculation based on the assumption can explain the particularly large permittivity of PMN.[10]

For normal ferroelectrics such as $BaTiO_3$, the nature of dielectric nonlinearity at different

ac drives has been universally accepted, i. e., the nonlinearity is caused by the movement of domain walls among the ferroelectric domains with different polarization directions. For relaxor ferroelectrics, opposite with normal ferroelectrics, no macro phase transition takes place, and no ferroelectric domain with micrometric dimensions appears. Under the usual conditions, the nanoscaled polar microregions in relaxors do not grow into ferroelectric domains even if the temperature is much lower than T_{max} (the temperature where the permittivity reaches a maximum). Therefore, it is greatly interesting to investigate the connections between the dielectric nonlinear response and the polar microregions.

The low frequency dielectric properties of PMN at different ac drives were first reported by Bokov et al. in the early 1960s.[11] But there have been little works reported on this subject until 1990s. In the recent decade, with the widely application of PMN-type relaxors and the increasing interests on the polarization mechanism of relaxors, the research of nonlinearity was emphasized again. Experiments showed that T_{max} shifts to lower temperature with increasing ac drive amplitude for PMN.[12,13] And the case of PLZT with relaxor behavior is similar.[14,15] The curves of permittivity at various drives are similar to the frequency dispersion in relaxors. Glazounov et al.[12] presented that the nonlinear behavior was controlled by the domain wall motion rather than the reorientation of polar clusters (i. e., superparaelectric approach[9]). However, they did not explain neither the type of domains nor the process of domain wall motion. Colla et al.[16] investigated the experiments of PMN-PT single crystals and pointed out that the nonlinearity mechanism is related to the drive amplitude: a glass-like dynamics of the polarization freezing process is dominant at low drives; at intermediate drives, the movements and reconstruction of the boundaries of polar nanodomains take place; at higher drives, the interactions between polar regions cause the formation of normal micron-sized domains and the movement of domain walls.

In this paper, the nonlinear dielectric response of 0.9PMN-0.1PT ceramics at various ac drive amplitudes and frequencies was studied. The experimental results were qualitatively explained by the phase transition theory of ergodic space shrinking in succession, and a Monte Carlo simulation was conducted to verify the theory.

II. EXPERIMENTAL PROCEDURE

0.9PMN-0.1PT powder was prepared by the columnbite precursor method.[17] The starting materials are analytically pure PbO, Nb_2O_5, TiO_2, and $(MgCO_2)_4.Mg(OH)_2.6H_2O$. $MgNb_2O_6$ was synthesized by $(MgCO_2)_4.Mg(OH)_2.6H_2O$ and Nb_2O_5 at 1000 °C. $MgNb_2O_6$, PbO, and TiO_2 powders were mixed and calcined at 870 °C for 2 h. Then the PMN-PT powders obtained were pressed into pellets ($\phi 10\times 1$–2 mm) at 100 MPa, and sintered in the PbO-rich atmosphere for 2 h at 1200 °C. The specimen were analyzed by the X-ray diffraction technique on a diffractometer (Science D/max-RA) using CuK_α raciation, and a pure perovskite structure was confirmed. Finally, the specimen were polished to 0.4 mm, and plated by silver. The dielectric permittivity was measured using a HP4284 LCR meter over the frequency range 1–100 kHz at a heating rate 3 K/min. The amplitude of the ac measuring field is 0.05, 0.25, 0.40, and 0.50 kV/cm.

III. RESULTS AND DISCUSSIONS

The usual amplitude of the ac signal used to measure the dielectric permittivity of relaxors is 0.01 kV/cm.[12] The results obtained correspond to the slope of the hysteresis loop, $\partial P/\partial E$, at the starting point. Because the amplitude is small enough to fall in the linear-response region, $\partial P/\partial E$ is constant, which represents the dielectric permittivity ε', i. e., the ε' value is independent on the amplitude of external field. However, with the increasing of ac field amplitude, the nonlinear terms can not be ignored.

Fig.1–Fig.3 show the change in the dielectric permittivity measured at various amplitudes when the ac field frequency is 1 kHz, 10 kHz and 100 kHz, respectively. From the figures one can list the following features: (1) when the measuring frequency is fixed, the dielectric permittivity keeps constant for various ac drives at high temperatures, while it increases with increasing the ac amplitude at low temperatures; (2) with increasing the amplitude, the dielectric permittivity maximum, ε'_m, increases and shifts to lower temperature; (3) the

diffusion behavior is more evident at larger ac amplitude; (4) the dielectric nonlinear effect is weakened at lower frequencies. Fig. 4 demonstrates the dielectric permittivity at various frequencies when the amplitude is fixed as 0.05 kV/cm. (The curves for $E = 0.25$, 0.4 and 0.5 kV/cm are omitted since they are similar to Fig.4.) It is noted that increasing amplitude has the same effects on the permittivity as decreasing frequency.

It can be seen from the results above that the effect of ac field amplitude on the permittivity maximum ε'_m is obvious. The relation between ε'_m and amplitude is depicted in Fig. 5. A linear law is found in the range of amplitude and frequency under study, which is consistent with the results of single crystal.[16] With increasing the frequency, the effect of amplitude on ε'_m is weakened. Extrapolate the curves in Fig. 5 to the zero field, we can obtain the permittivity maximum without nonlinear effect. Table I gives the variation of ε'_m when the amplitude increases from 0.05 kV/cm to 0.5 kV/cm. It shows that ε'_m increases by 7.4% at 1 kHz (which is the frequency in usual measurements). This means that the measuring result of permittivity is affected by the weak-field nonlinearity. As a result, the thickness and the applied voltage of specimen, i. e., the field strength, should be specified to avoid the influence of nonlinear effect, so that the results in different experiments are comparable.

It was mentioned in Sec. I that there were different explains on the nonlinear effect at weak fields.[12,16] Glazounov et al.[12] denied the mechanism of reorientation of polar clusters, but they have ignored the interactions between polar clusters. Colla et al.[16] presented that a glass-like dynamics of the polarization freezing process dominates at low drives. However, the connections between the dynamic process and the nonlinear effect were not explained.

We proposed that the dielectric nonlinearity of relaxor ferroelectrics at low drives, as well as the frequency dispersion, can be explained in the theory of the phase transition of ergodic space shrinking in succession.[18] The TEM dark-field image of 0.9PMN-0.1PT proved that there are a great amount of nanoscaled ordered microregions embedded in the disordered matrix.[19] At a certain temperature, the homogeneous crystal structure of the ordered microregions causes the cooperative displacement of B-site cations along one

of eight $\langle 111 \rangle$-equivalent directions. When the temperature is high enough, the thermal energy, $k_B T$, is much larger than the energy barriers between different directions, which results that the probabilities of displacement along eight directions are equal, i. e., the system is ergodic. Thus the ordered microregions are unpolar. However, the environments of the microregions along different directions are not identical, and the spherical symmetry of ordered microregions breaks down. Since the potential wells of different $\langle 111 \rangle$ directions are different, the B-site ions tend to stay along the direction with the lowest well for more time in the thermal flipping process when the temperature decreases to a certain value. Thus the ordered microregions transform into the polar microregions, and dipole behavior appears. Due to the cooperative displacement, the ions in the same microregion flip as a whole unit under external drives, so the dielectric permittivity of relaxor ferroelectrics is extraordinarily high. The polar microregions are random the magnitude and direction of polarization. Under zero field, $\sum p_i = 0$, while $\sum p_i^2 \neq 0$. When the temperature is much higher than the freezing temperature, the relaxation times of polar microregions are much shorter than the observation time. All the polar microregions flip dynamically with ac drives, so the sum of polarizations, P, is proportional to the external field, i. e., the dielectric permittivity, $\varepsilon = \partial P / \partial E$, is independent on the frequency and the amplitude of external field. In this temperature range, the deviation of micro-polarization direction from that of external field by thermal fluctuation is weakened with decreasing temperature, and then the permittivity increases with decreasing temperature. This corresponds to the high temperature regions in Fig.1–Fig.4, where no frequency dispersion and nonlinearity is found. The polar microregions can be regarded as independent dipoles. When the temperature further decreases, the electrostatic interactions between dipoles get more and more strong. Under the ac drives with a certain frequency, the flip of a dipole is affected by both the external field applied and the internal field generated by other dipoles. Some dipoles cannot keep up with the switching of the measuring field, and become "slow dipoles". Some are even frozen along a certain direction, and become "frozen dipoles". Thus the phase space with ergodicity is shrinking in succession. When the frequency increases, the time scale

of dipole flipping is shortened. More dipoles cannot reach the equilibrium states in the observation time, i.e., the proportion of slow dipoles and frozen dipoles increases. Slow dipoles and frozen dipoles give no or little contribution to the flipping polarization. So the dielectric permittivity decreases, which is the frequency dispersion in relaxors. When the ac field amplitude increases, the driving force on dipoles is enhanced. Slow dipoles and frozen dipoles are forced to flip faster and give more contribution to the flipping polarization. The proportion of slow dipoles and frozen dipoles decreases, and the dielectric permittivity increases, which is the nonlinear effects in relaxors. This is the origin of the special dielectric properties in relaxors (frequency dispersion, nonlinearity, etc.).

It should be emphasized that the external field discussed above is in the range of weak drives (less than 0.6 kV/cm according to Ref. 16). Only at weak drives can nanoscaled dipoles exist, and the long-range interactions between dipoles dominate in the dynamic process. If the external field increases, motions and reconstruction of the boundaries of polar nanodomains would take place. Under the strong fields, through interacting with the disordered matrix surrounding, polar nanodomains will switch, coalesce, and grow into the conventional micron-sized ferroelectric domains as that in normal ferroelectrics.[16,20] Then the model discussed above is not applicable to describe the polarization dynamics.

In order to better understand the dielectric nonlinearity in relaxors and verify the model above, a Monte Carlo simulation is conducted in the next section to investigate the dynamic flipping process of the polar microregions .

IV. MONTE CARLO SIMULATION

Gui et al.[21] have used the Monte Carlo method to simulate the dynamics of freezing process in relaxor ferroelectrics. In the theory framework of Ref. 21, the polar microregions are modeled as point dipoles. The interaction between two dipoles with moment $\vec{\mu}_i$ and $\vec{\mu}_j$ is expressed as

$$J_{ij} = J_{ji} = -\vec{\mu}_j \cdot \frac{1}{4\pi\varepsilon_0} \left(\frac{3\,\vec{\mu}_i \cdot \hat{r}_{ij}}{r^3} \hat{r}_{ij} - \frac{\vec{\mu}_i}{r^3} \right)$$

$$= -\frac{1}{4\pi\varepsilon_0} \cdot \frac{3\cos\varphi_i \cos\varphi_j - \cos\phi}{r^3}\mu_i\mu_j, \tag{1}$$

where $\hat{r}_{ij}$ is the unit vector between the two dipoles. r is the distance between dipoles. φ_i (φ_j) is the angle between $\vec{\mu}_i$ $(\vec{\mu}_j)$ and $\hat{r}_{ij}$. ϕ is the angle between $\vec{\mu}_i$ and $\vec{\mu}_j$. The Hamiltonian of relaxors at dc bias is obtained as

$$H = \frac{1}{2}\sum_{i\neq j} J_{ij} - E\sum_i \mu_i \cos\theta_i, \tag{2}$$

where E is the dc field strength. θ_i is the angle between $\vec{E}$ and $\vec{\mu}_i$.

The effective interaction energy, $\tilde{J}_{ij}$, is introduced as

$$\tilde{J}_{ij}\, \sigma_i\sigma_j = J_{ij}\mu_i\mu_j/2, \tag{3}$$

where $\sigma_i = \pm 1$ is the projection of $\vec{\mu}_i$ on the direction of the external field. Eq. (2) can be rewritten as

$$H = -\sum_{i\neq j} \tilde{J}_{ij}\, \sigma_i\sigma_j - E\overline{\mu}\sum_i \frac{|\mu_i \cos\theta_i|}{\overline{\mu}}\sigma_i, \tag{4}$$

where $\overline{\mu}$ is the maximal projection of dipole moments on the external field.

Ref. 21 used Eq. (4) to study the dielectric origins of relaxor ferroelectrics under dc external field. It is unsuitable for the case of ac field. However, the polarization mechanism should be similar in both ac and dc fields. Therefore, an ac field term is introduced as

$$E(t) = E \cos\left(2\pi\frac{t}{t_L}\right), \tag{5}$$

where t_L is the period of the ac field, which corresponds to the frequency. Thus a Hamiltonian similar to Eq. (4) is obtained:

$$H = -\sum_{i\neq j} \tilde{J}_{ij}\, \sigma_i\sigma_j - E(t)\overline{\mu}\sum_i \frac{|\mu_i \cos\theta_i|}{\overline{\mu}}\sigma_i. \tag{6}$$

A Gaussian distribution is assumed for $\tilde{J}_{ij}$, i. e.,

$$P(\tilde{J}_{ij}) \propto exp[-\frac{\tilde{J}_{ij}^{\,2}}{2(\Delta J)^2}], \tag{7}$$

where ΔJ is the distribution width.

There are N dipoles in the system. (N=$16 \times 16 \times 16$) The flipping probability of the ith dipole is defined as

$$W = \frac{1}{e^{\delta H/k_B T} + 1},\tag{8}$$

where δH is the change of energy when the dipole flip from σ_i to $-\sigma_i$. The details of simulation process can be found in Ref. 21. Then the ac permittivity can be obtained as

$$\chi = \frac{1}{E} \cdot \frac{1}{t_{obs}} \int\limits_{t_0}^{t_0+t_{obs}} p(t) \exp\left(i2\pi\frac{t}{t_L}\right) dt,\tag{9}$$

where $p(t)$ is the average polarization.

Fig. 6 shows the temperature dependence of dielectric permittivity at various ac amplitudes when the frequency is fixed as t_L=5 MCS/dipole. It can be seen that the diffusion behavior is enhanced with increasing amplitude. The simulation results are consistent with experiments in main features, which verifies the polarization mechanism described by the above model. It is noted that the curve of E=$3.0\Delta J/\overline{\mu}$ (which corresponds to a stronger field) lies below other curves at high temperatures. In this case, maybe the corresponding field is too strong and cause the growth of dipoles, so the weak-field model is not applicable.

V. CONCLUSIONS

The dielectric nonlinear response of 0.9PMN-0.1PT ceramics was revealed over the field range 0.05–0.50 kV/cm. When the measurement frequency is fixed, the dielectric permittivity is invariant with field amplitude at high temperatures. At low temperatures, the permittivity maximum, ε'_m, increases and shifts to lower temperatures with increasing amplitude. A linear law between ε'_m and the amplitude was observed at all frequencies and amplitudes in the experiment. The nonlinearity is weakened at higher frequencies. The effects of increasing amplitude are similar to that of decreasing frequency. It was proposed that the nonlinearity of relaxors at low drives can be explained in the theory of the phase

transition of ergodic space shrinking in succession. A Monte Carlo simulation was conducted to investigate the dynamic flips of polar microregions at low drives and verify the proposition.

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TABLES

TABLE I. The variation of dielectric permittivity maximum when the amplitude increases from 0.05 kV/cm to 0.5 kV/cm.

frequency (kHz)	change of ε_m (%)
1	7.4
10	6.4
100	2.0

FIGURES

FIG. 1.   The dielectric permittivity of 0.9PMN-0.1PT as functions of temperature at various amplitudes when the frequency is fixed as 1 kHz.

FIG. 2.   The dielectric permittivity of 0.9PMN-0.1PT as functions of temperature at various amplitudes when the frequency is fixed as 10 kHz.

FIG. 3.   The dielectric permittivity of 0.9PMN-0.1PT as functions of temperature at various amplitudes when the frequency is fixed as 100 kHz.

FIG. 4.   The dielectric permittivity of 0.9PMN-0.1PT as functions of temperature at various frequency when the amplitude is fixed as 0.05 kV/cm.

FIG. 5.   The dielectric permittivity maximum of 0.9PMN-0.1PT at various amplitudes and frequencies.

FIG. 6.   The simulation results of dielectric permittivity at various amplitudes when t_L=5MCS/dipole. The temperature is measured in unit of $\Delta J/k_B$, and amplitude in unit of $\Delta J/\overline{\mu}$.